Combustion Characteristics of Condensed Phase Reactions in Sub-Centimeter Geometries

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ABSTRACT

In this work, the combustion characteristics of the exothermic systems Ti/C, Ni/Al, 3Ni/Al and combinations thereof, are examined in small diameter aluminum tubes (3–6 mm ID). Tailoring the overall exothermicity of the reactant system is accomplished by varying the reaction combination, stoichiometry, and the addition of alumina as a diluent. For the combined reactive system, Ti/C-3Ni/Al, it is shown that at 40 wt.% Ti/C content, the failure diameter lies between 3 and 4 mm. While at a Ti/C content of 30 wt.%, complete combustion front propagation is only observed for tube diameters of 6 mm. For the more exothermic system, Ti/C-Ni/Al, studied at a diameter of 4.8 mm, the addition of low levels of alumina as a diluent is shown to drastically alter the combustion front velocity, resulting in extinction with an increase from 2 to 2.5 wt.% addition. The addition of a thermal barrier (Grafoil™) for Ti/C-Ni/Al (15/85 wt.%) diluted with 2 wt.% Al_2O_3, results in an increase in propagation rate and the range of packing densities that complete propagation is observed; the effects of Grafoil™ on the reactive composition Ti/C-3Ni/Al (35/65 wt.%) are not as pronounced.

Introduction

While the combustion characteristics of various condensed phase reactions have been widely investigated for the large scale production of a number of ceramic and intermetallic materials, they have not typically been studied in small diameter channels (e.g. less than 6 mm). At these sizes, high heat losses can dominate (particularly for metal channels) leading to combustion front instabilities (oscillations, pulsating, etc.) or extinction. Reactive systems that are characterized as having high activation energies and which are strongly exothermic, such as Ti/C (ΔH_f = -3080 J/g [1]), Ti/B_4C (ΔH_f = -3610 J/g [2]), and Ti/2B (ΔH_f = -5520 J/g [1]), may be ideal for overcoming the high heat losses present in such sub-cm metal channels (e.g. delay elements, igniters, etc.). In these cases, the combustion process may be completed due to a relatively low ratio of heat loss to heat generation in the combustion zone. For example, Pacheco et al. [3] studied Ti/2B and Ti/C with Cu and Al diluents and showed no diameter effect on reaction rate until extinction at diameters as small as 6.48 mm. In a pellet configuration, Roy and Biswas [4] studied Ti/2B and Ti/B and showed that diameters below 6 mm would quench.

At the very small scale (sub-mm), Tappan et al. [2] conducted experiments of the Ti/B_4C system with diluent/binder (Ni/Al) in borosilicate glass capillaries ranging from ~0.4 to 1.0 mm internal diameter showing that a steady reaction can propagate even at diameters as small as 0.4 mm. Their work also showed that there was no significant decrease in combustion front velocity with decreasing capillary size.

In the case where Ti/C is combined with diluents, such as Ni or Al, or the combination of Ni/Al, the reaction is known to proceed by first forming a melt zone comprised of Ti and Ni or Al. The

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14. ABSTRACT
In this work, the combustion characteristics of the exothermic systems Ti/C, Ni/Al, 3Ni/Al and combinations thereof, are examined in small diameter aluminum tubes (36 mm ID). Tailoring the overall exothermicity of the reactant system is accomplished by varying the reaction combination, stoichiometry, and the addition of alumina as a diluent. For the combined reactive system, Ti/C-3Ni/Al, it is shown that at 40 wt.% Ti/C content, the failure diameter lies between 3 and 4 mm. While at a Ti/C content of 30 wt.%, complete combustion front propagation is only observed for tube diameters of 6 mm. For the more exothermic system, Ti/C-Ni/Al, studied at a diameter of 4.8 mm, the addition of low levels of alumina as a diluent is shown to drastically alter the combustion front velocity, resulting in extinction with an increase from 2 to 2.5 wt.% addition. The addition of a thermal barrier (GrafoilTM) for Ti/C-Ni/Al (15/85 wt.%) diluted with 2 wt.% Al2O3, results in an increase in propagation rate and the range of packing densities that complete propagation is observed; the effects of GrafoilTM on the reactive composition Ti/C-3Ni/Al (35/65 wt.%) are not as pronounced.

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remaining metal reactants then diffuse into the melt layer and exothermically react to form the next melt layer by which the reaction proceeds [5]. However, if the heat losses (increasing with decreasing diameter) in the reaction zone are too high relative to the heat generated, the next reaction layer may experience instabilities or extinction. In order to utilize these types of reactions in sub-cm geometries it is critical to understand the relationship between heat generation and system heat losses if combustion instability and extinction are to be avoided.

In this work, combinations of the well known systems Ti/C, Ni/Al and 3Ni/Al are studied in 3 to 6 mm diameter aluminum tubes. By combining the highly exothermic Ti/C reaction with the less exothermic reactions of Ni/Al or 3Ni/Al, the effect of overall mixture exothermicity on combustion front propagation is observed. Further, the role of packing density, mixture stoichiometry, reaction combinations, thermal barriers (radial) and inert dilution on the combustion characteristics are presented.

Experimental

Thermochemical Calculations

The HSC7.0 Chemistry program was used to predict the adiabatic temperatures for the condensed phase reactions Ti/C, Ni/Al, and 3Ni/Al. Several other thermochemical codes (Cheetah v6.0 [6], NASA CEA [7] and "thermo program" [8]) were considered but ultimately not used due to insufficient thermochemical and product libraries for such reactions. Adiabatic temperatures were predicted assuming no intermediate phases and no phase changes due to the available product libraries within HSC7.0. Therefore, a relative comparison between systems can be made but the predicted values should not be viewed as the expected experimental combustion temperatures.

Compositions

Nominal sizing and vendor information for the powders used in these experiments are summarized in Table 1. The mixtures for the reactive composition Ti/C-3Ni/Al (Novamet Ni) were dry mixed using a Resodyn LabRAM acoustic mixer at 80% intensity in two minute intervals for a total of 6 minutes. The mixtures for the reactive composition Ti/C-Ni/Al-Al_2O_3 (Alfa Aesar Ni) were prepared via mortar and pestle simply for screening purposes.

Table 1. Powder information

Powder	Vendor	Nominal Size
Al	AAE	1-5 μm
C (Lamp Black)	Spectrum Chemical	sub-μm
Ni	Alfa Aesar	1-5 μm
Ni	Novamet	3-11 μm
Ti	Alfa Aesar	-325 mesh
Al_2O_3	Novacentrix	40 nm

Combustion Experiments

The experimental tubes used were made from 2024 grade T3 Aluminum, with inner (outer) diameters of 3 mm (8.54 mm), 4 mm (8.94 mm), 4.8 mm (9.32 mm) and 6 mm (10.00 mm). These dimensions were selected to keep the thermal mass of the aluminum tube the same for all of the different diameters. The average mass of the tubes (regardless of diameter) was 2.126 grams with a standard deviation of 0.005 grams. In some cases, a 0.254 mm graphite foil (Grafoil^{TM}) liner was inserted into the tube. Grafoil^{TM} was supplied by Mineral Seal Corporation. Reactive compositions were pressed to a stop into the aluminum tubes using a Carver 12 ton press so that select packing densities could be achieved. Approximately 1 mm of A1A was pressed on either end of the aluminum tube at a packing density of 3.0 g/cm^3. The experimental configuration is shown in Fig. 1. The experiments were recorded using a digital video camera at 30 fps. The A1A was ignited with 30 gauge NiChrome wire and the reported system propagation rate was determined by the length of the tube divided by the time between first light (A1A ignition) on either side of the aluminum tube.

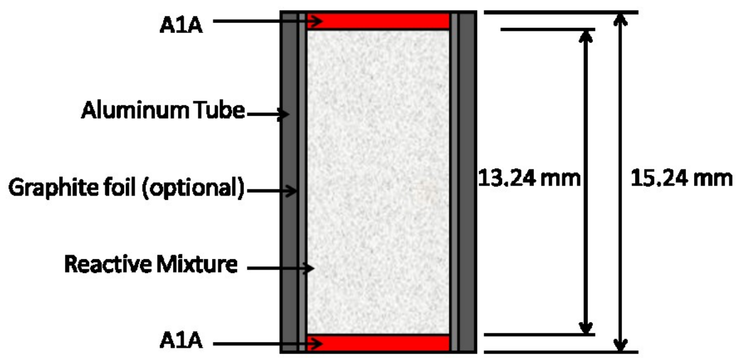


Figure 1. Experimental configuration for packed combustion experiments.

Results and Discussion

Thermo-chemical Considerations

The strongly exothermic reaction of Ti/C combined with the less exothermic reactions of Ni/Al or 3Ni/Al, creates a system with tailored exothermicity based on the relative ratios of each reactive system. A summary of the adiabatic reaction temperatures and heats of formation for these individual reactions are presented in Table 2. By tailoring the exothermicity of the composition, we can manipulate the ratio of heat loss to heat generation to avoid reaction extinction.

Table 2. Adiabatic reaction temperatures and predicted heats of formation

Reaction	Adiabatic Reaction Temperature (K)	Heat of Formation (J/g)
Ti/C	3210 [9]	-3080
Ni/Al	1910[9]	-1560*
3Ni/Al	1524[1]	-750

*Note that the value calculated from HSC7.0 for Ni/Al differs from that reported in the literature (-1380 J/g) [1]. All calculations reported for ΔH_f are from HSC7.0 for the sake of consistency.

Two methods of modifying the combustion temperature were considered in this work: i) altering the stoichiometry from Ni/Al to the less exothermic/lower combustion temperature reaction of 3Ni/Al and ii) adding diluent with an inert (Al_2O_3). The calculated adiabatic combustion temperatures for the combined reactive compositions Ti/C-Ni/Al and Ti/C-3Ni/Al are presented in Fig. 2. There is a significant drop in predicted adiabatic combustion temperature between 30 wt.% < Ti/C < 40 wt.% for the Ti/C-3Ni/Al composition. This is the region that was targeted as we expect the slowest reaction propagation, which would allow us to assess the failure diameters more readily. For the system based on the more exothermic reaction Ni/Al, Ti/C(15 wt.%)-Ni/Al(85 wt.%) was selected due to a moderate predicted adiabatic combustion temperature (1965 K) and heat of formation (ΔH_f = -1790 J/g). This reactive composition, hereafter referred to as Ti/C-Ni/Al(15/85), was then diluted with low levels of alumina (Table 3) to slow the combustion propagation rate. Preliminary combustion experiments in 4.8 mm diameter tubes showed that increasing the diluent level from 2 to 2.5 wt.% alumina resulted in reaction extinction. Therefore, for the sake of this study Ti/C-Ni/Al(15/85) diluted with 2 wt.% alumina was the composition used.

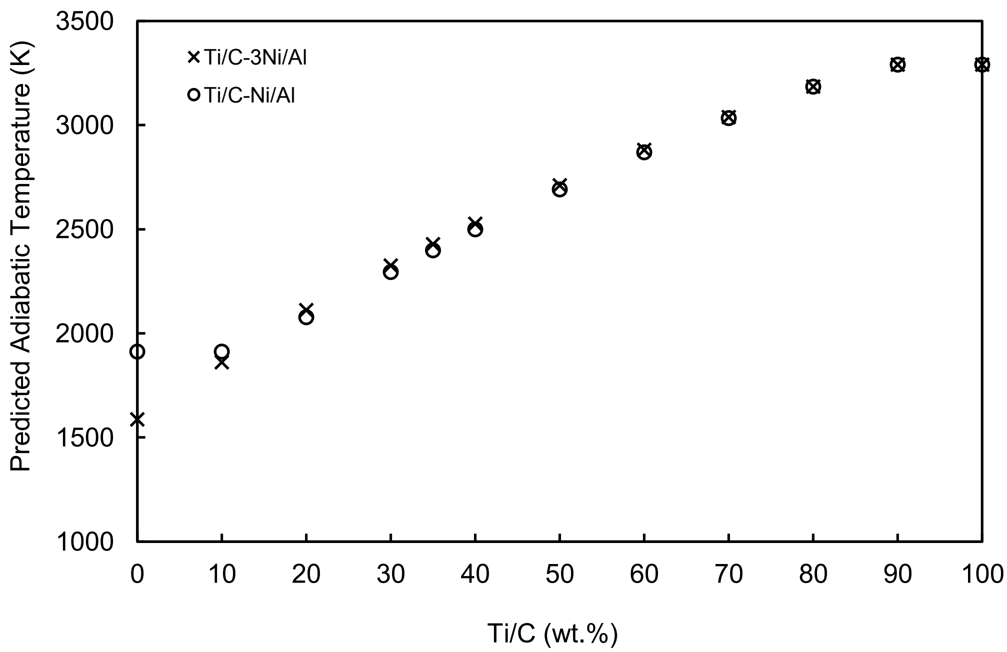


Figure 2. Predicted adiabatic reaction temperature vs. Ti/C content.

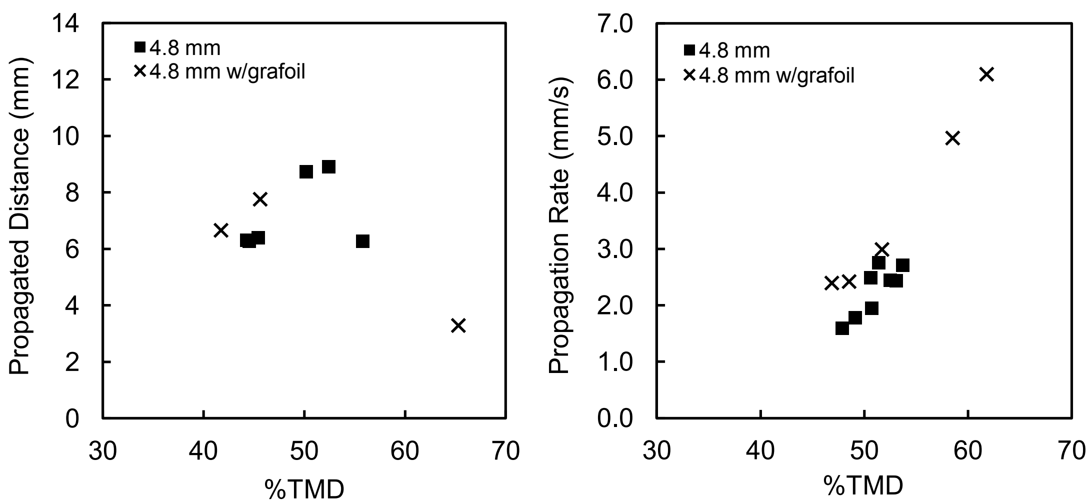
Table 3. Predicted adiabatic reaction temperatures and heats of formation for Ti/C-Ni/Al(15/85 wt.%) with Al_2O_3 dilution

Reactive Composition	Predicted Adiabatic Reaction Temperature (K)	Predicted Heat of Formation (J/g)
Ti/C-Ni/Al(15/85)	1965	-1790
Ti/C-Ni/Al(15/85) -Al_2O_3(1 wt.%)	1942	-1770
Ti/C-Ni/Al(15/85) -Al_2O_3(2 wt.%)	1918	-1750
Ti/C-Ni/Al(15/85) -Al_2O_3(2.5 wt.%)	1912	-1740

Combustion Results

It is well known for condensed phase reactions that packing density strongly influences the combustion front velocity [9]. There is a lower packing density at which the reactant compact is highly porous and thermal energy generated from the reaction is not able to be transferred to the next layer, resulting in combustion extinction. In contrast, at higher densities the thermal conductivity of the compact can cause sufficient heat to be conducted away from the reaction zone resulting in quenching.

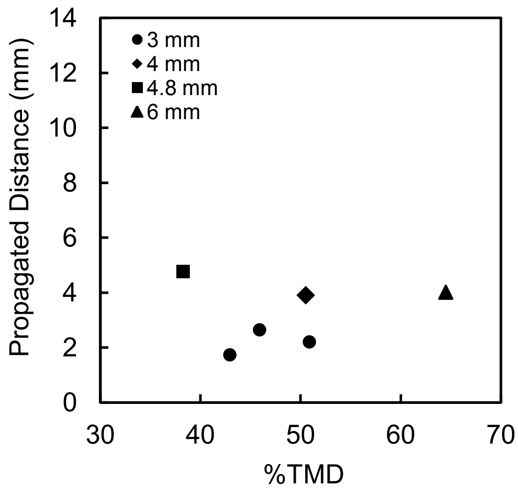
The effect of packing density, in terms of percent theoretical maximum density (TMD), on the combustion front propagation for the Ti/C-Ni/Al(15/85) diluted with 2 wt.% Al_2O_3 (-1750 J/g) is presented in Fig. 3. As previously discussed, dilution of this system with 2 wt.% alumina lowers the predicted combustion temperature to 1918 K; this is approaching the recommended cutoff temperature (1800 K) for self propagating reactions [10]. Therefore, we expect this reactive composition to have a very slowly propagating combustion front or to simply self extinguish. For this study, the 4.8 mm ID aluminum tube was selected as the baseline. We observe a range of packing densities (47 to 54% TMD) where the reaction fully propagates the length of the tube. Notably, there were two experiments conducted in this range where extinction was observed. For this particular system, the heat losses are large enough relative to the heat generated that extinction is not surprising, particularly since the predicted adiabatic combustion temperature is so low. To reduce the heat losses, a Grafoil™ thermal barrier was implemented. This reduction in heat losses has several beneficial effects on the overall stability and reaction rate. First, the overall propagation rate increases along with the range of packing densities we observe full propagation (47 to 62% TMD) and no partial propagations were observed. This is in spite of a reduction in effective diameter and hence less reactive composition, resulting in ~206 J less of potential chemical energy when compared to the baseline diameter at 50% TMD.



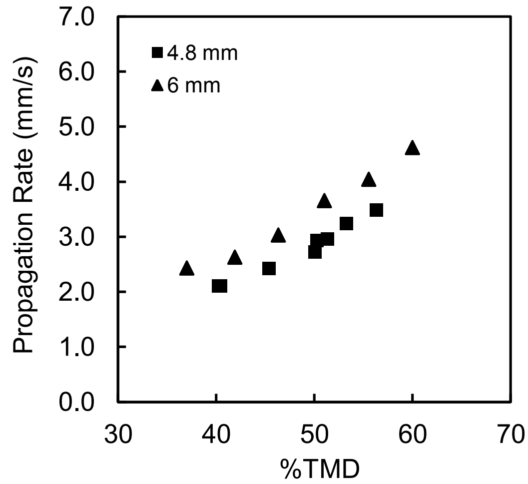
(a) (b)

Figure 3. Propagated distance (a) and propagation rate (b) for Ti/C-Ni/Al(15/85 wt.%) diluted with 2 wt.% Al_2O_3. Note that for propagated distance only partial propagations are plotted for clarity. Full propagation distance is 13.29 mm.

For these experiments, Ni/Al was replaced with the less exothermic reaction 3Ni/Al. A reactive composition of Ti/C(35 wt.%)-3Ni/Al(65 wt.%) (-1570 J/g), hereafter denoted as Ti/C-3Ni/Al(35/65), was chosen as the baseline composition. This was based on a favorable exothermicity and a predicted adiabatic combustion temperature of 2428 K (well above 1800 K). It is noted that the slowest of each of these reactive compositions that do not quench in the 4.8 mm diameter aluminum tube have very different predicted heats of formation and adiabatic temperatures (-1570 J/g and 2428 K vs. -1750 J/g and 1918 K). This demonstrates the importance of selecting a reactive system where the overall heat generation of the reaction can overcome the system heat losses. Figure 4 shows the effect of diameter and packing density on the combustion of this reactive mixture. At a diameter of 3 mm, the reaction propagated 2 to 4 mm, while at a diameter of 4 mm, 50% TMD, the sample propagated 3.9 mm before extinction. Therefore, the failure diameter is between 4 and 4.8 mm. Lastly, when increasing the initial diameter of the sample from 4.8 to 6 mm, there was an overall increase in reaction rate and range of packing densities where full propagation resulted (Fig. 4b).



(a)



(b)

Figure 4. Propagated distance (a) and propagation rate (b) for Ti/C-3Ni/Al(35/65wt.%). Note that for propagated distance only partial propagations are plotted for clarity. Full propagation distance is 13.29 mm.

In this reactive composition, the effect of Grafoil™ lining is illustrated in Fig. 5. In contrast to the reactive composition Ti/C-Ni/Al(15/85) diluted with 2 wt.% Al_2O_3, less of a dramatic effect was observed. This is likely due to a higher predicted adiabatic combustion temperature of 2428 K (well above 1800 K). When comparing the 6 mm case with and without Grafoil™, little difference was observed in both the propagation rate and overall range of packing densities that full propagation occurred. At 4.8 mm, the Grafoil™ lined cases had a noticeably smaller range of packing densities at which the reaction fully propagated (45 to 50% TMD). Two of three experiments conducted at 55% TMD did not fully propagate, which indicates that the failure diameter is being approached. For this system, the added benefits of reducing the radial heat loss to the tube via Grafoil™ are effectively canceled out by the small (0.46 mm) decrease in tube diameter (less reactive composition). For example, at 50% TMD, the addition of the thermal barrier effectively reduces the potential chemical energy of the system by ~184 J and ~230 J at 4.8 and 6 mm respectively.

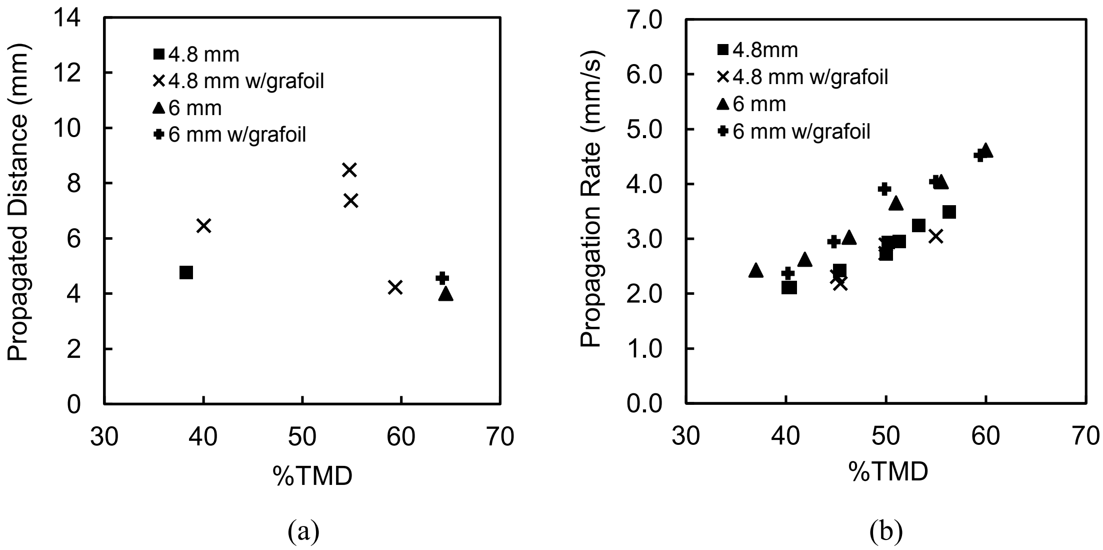
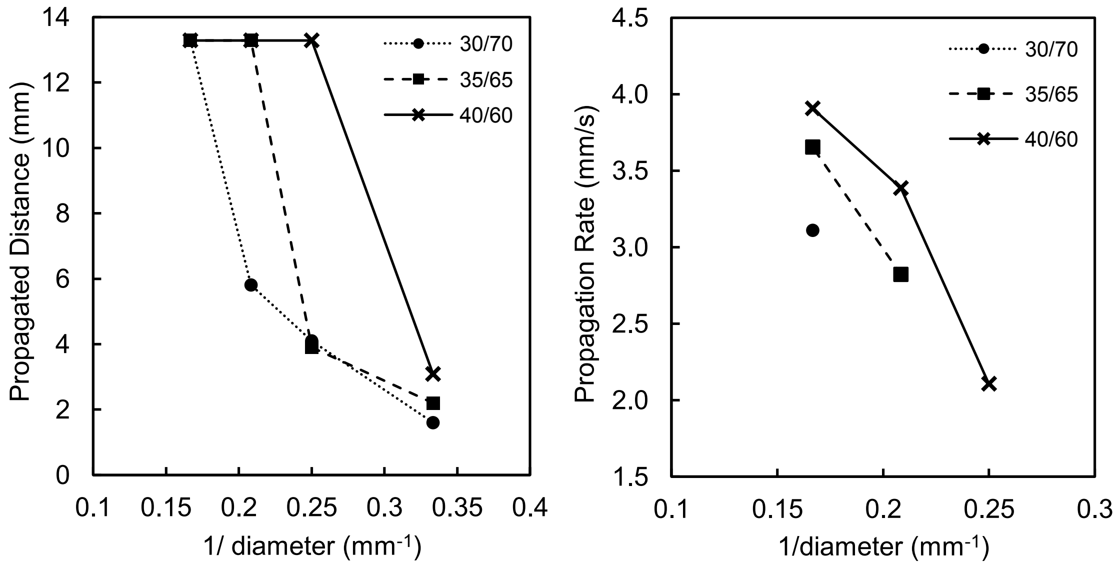


Figure 5. Propagated distance (a) and propagation rate (b) for Ti/C-3Ni/Al(35/65 wt.%) with and without Grafoil^{TM}. Note that for propagated distance only partial propagations are plotted for clarity. Full propagation distance is 13.29 mm.

Lastly, the effect of modifying the reaction exothermicity with Ti/C content was examined for varying tube diameter. Figure 6 shows a series of Ti/C-3Ni/Al experiments all at 50% +/-1% TMD presented as a function of inverse tube diameter. As previously discussed, the system Ti/C-3Ni/Al(35/65) (-1570 J/g) ceased to fully propagate between 4 and 4.8 mm. By increasing the Ti/C content by 5 wt.% (-1680 J/g), the reaction is now exothermic enough to fully propagate at a diameter of 4 mm whereas the baseline composition was not. Furthermore, decreasing the Ti/C content by 5 wt.% reduces the exothermicity (-1450 J/g) so that the reactive composition does not fully propagate at 4.8 mm whereas the baseline did. The Grafoil^{TM} lined case, at 35/65, has a failure diameter between 3.6 and 4.4 mm in comparison to the baseline failure diameter between 4 and 4.8 mm. This illustrates that these reactive systems can be tailored to propagate at various diameters, and at selected velocities, for a given application (igniters, delay fuses, etc.). More data is required to draw further conclusions about the effect of thermal barriers on failure diameter.



(a) (b)

Figure 6. Propagated distance (a) and propagation rate (b) as a function of Ti/C-3Ni/Al composition ratio.

Summary and Conclusions

In this work the combustion characteristics of the exothermic systems Ti/C, Ni/Al, 3Ni/Al and combinations thereof, were examined in small diameter aluminum tubes (3–6 mm ID). We have demonstrated the ability to alter the overall exothermicity of the reactant system by varying the reaction combination and stoichiometry resulting in a range of propagation times. By varying packing density, the addition of inert diluents or by the use of a thermal barrier (Grafoil^{TM}), further tailoring for a specific application is possible. For example, for Ti/C-3Ni/Al, it was shown that by varying the Ti/C content, the system can be tailored to propagate at various diameters and at selected velocities. For the more exothermic system Ti/C-Ni/Al(15/85), the addition of alumina as a diluent was shown to result in failure when alumina is increased from 2 to 2.5 wt.% addition. For the reactive composition Ti/C-Ni/Al(15/85) diluted with 2 wt.% Al_2O_3, Grafoil^{TM} increases the propagation rate and the range of packing densities we observe complete propagation; the effects of Grafoil^{TM} on the reactive composition Ti/C-3Ni/Al(35/65) were not as pronounced. Further work remains to quantify the experimental heat losses to the aluminum tube and how those losses induce pulsations, oscillations or are responsible for reaction extinction.

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